

SOUTHWEST CATALYSIS SOCIETY



2009 SPRING SYMPOSIUM

April 24, 2009

Duncan Hall

Rooms 1042, 1075 (poster rooms + sponsor displays + snacks)

Room 1070 (lecture room)

Rice University, Houston, TX

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The SWCS officers and I welcome you to the 2009 SWCS Spring Symposium, **April 24, 2009, Friday**, at Rice University, Houston, TX.

This annual regional meeting provides a forum where catalysis in its various forms – heterogeneous to homogeneous, computational to the experimental, surface science to materials synthesis, applied to fundamental, academic to industrial – can be discussed.

We are delighted to present 6 invited speakers and over 25 registered poster presentations for today's meeting. Meritorious posters presented by students and post-docs will be identified with **Best Poster Awards**, carrying cash prizes.

The 2009 Spring Symposium **registration fee is \$40**, which includes North American Catalysis Society and SWCS yearly membership dues and the coffee/snack breaks. To speed registration, provide your business card along with your registration fee. Do let those who cannot attend the Symposium know to mail in their membership due (\$25) to our Treasurer, Prof. George Stanley (mailing address shown at left). Unfortunately, we cannot take credit cards for payment.

Normally, students pay \$10 for registration (NACS and SWCS membership dues included). Due to the efforts of Prof. Kerry Dooley in securing funds from the North American Catalysis Society, we will waive registration fees for both students and postdocs this year, and we will also pay for lunch for students and postdocs.

Enjoy!

Michael Wong
Chair



FINAL PROGRAM

- 8:00 AM Registration – Prof. George Stanley (LSU)**
Duncan Hall Rm. 1075
- 8:30 AM Chair's Welcoming Remarks – Prof. Michael Wong (Rice)**
Duncan Hall Rm. 1070
- 8:45 AM Dr. Ruth M. Kowaleski (CRI/Criterion, Houston, TX)**
"Ethylbenzene Dehydrogenation Catalyst Development & Commercialization Utilizing High Throughput Experimentation"
- 9:15 AM Prof. Kenneth J. Balkus, Jr. (UT Dallas, Richardson, TX)**
"Titanium Dioxide Nanotube Composites for Photocatalysis"
- 9:45 AM Coffee Break (sponsored by Micromeritics and DCG Partnership) / Poster Setup**
Duncan Hall Rm. 1042 and 1075
- 10:15 AM Prof. Donghui Zhang (LSU, Baton Rouge, LA)**
"Catalytic Routes towards Well-Defined Poly- α -Peptoids"
- 10:45 AM Prof. Janet Bluemel (Texas A&M University, College Station, TX)**
"Immobilized Catalysts: New Insights by Solid-State NMR Spectroscopy"
- 11:15 AM Lunch Break (on your own) / Poster Preview**
Rice Student Center
- ~12:20 PM Return from lunch and re-assemble*
- 12:30 PM Dr. Z. Conrad Zhang (Kior Inc., Pasadena, TX)**
"Liquid Phase Catalytic Conversion of Cellulosic Biomass to Biofuels and Biobased Products"
- 1:00 PM Prof. Manos Mavrikakis (U. Wisconsin, Madison, WI)**
2009 Paul H. Emmett Award in Fundamental Catalysis
"The Importance of Nano-Architecture in Heterogeneous Catalysis"
- 1:45 PM Poster Session (sponsored by SABIC Americas and Shell) / Coffee Break (sponsored by Micromeritics and DCG Partnership)**
Duncan Hall Rm. 1042 and 1075
- 3:30 PM Poster Awards (sponsored by SABIC Americas and Shell) and SWCS Business**
- 4:00 PM Adjourn**



ETHYLBENZENE DEHYDROGENATION CATALYST DEVELOPMENT AND COMMERCIALIZATION UTILIZING HIGH THROUGHPUT EXPERIMENTATION

Ruth M. Kowaleski¹ and A. Lange de Oliveira²

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Keywords: Ethylbenzene Dehydrogenation Catalyst, Styrene Monomer Production

The use of high throughput testing tools at hte Company has enabled the CRI Catalyst Company ethylbenzene dehydrogenation catalyst research team to screen hundreds of new catalyst formulations in a short period of time. The strategy for identifying new catalyst formulation leads using high throughput experimentation and a comparison of high throughput testing and conventional catalyst testing will be presented.

In addition, the process for commercializing one of the promising formulations discovered in the early phases of the high throughput testing program at hte Company will be described. For example, during the course of the new catalyst commercialization process additional high throughput and conventional experimental testing work was carried out in order to optimize the performance responses of the initial formulation lead. Ultimately, an optimized catalyst formulation was successfully manufactured at scale and its superior performance characteristics validated experimentally.

The new commercial catalyst, AstraCat, is the first CRI US LP product developed utilizing high throughput testing methodology. It was introduced to customers in November 2007. Relative to older generations of ethylbenzene dehydrogenation catalysts, AstraCat exhibits significant performance advantages in terms of both activity and selectivity.

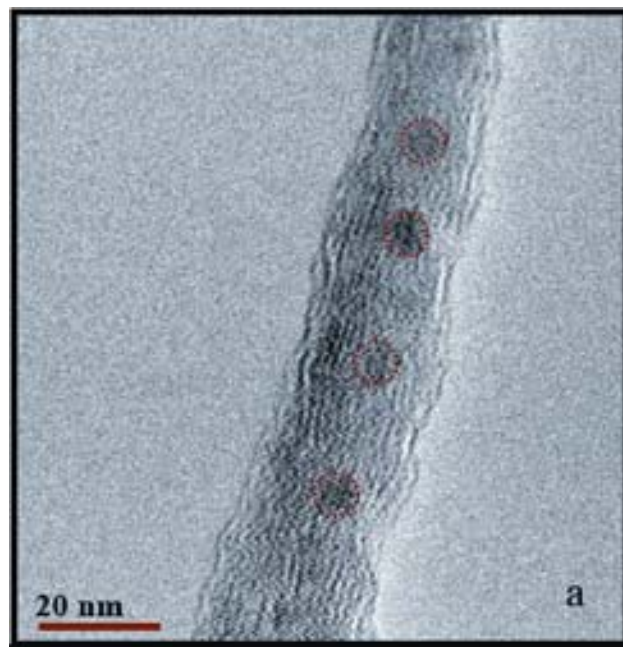
Ruth Kowaleski is a Sr. Staff Research Chemist at CRI Catalyst Company. She joined Shell in 1986 and worked in ethylene oxide catalyst development and manufacturing support for 11 years and on a catalyst recycling and metal reclamation project for 3 years. Since 2000 she has been working on ethylbenzene dehydrogenation catalyst development. She received a B.S. in Chemistry from Michigan State University in 1982, and a M.S. and Ph.D. in Inorganic and Organometallic Chemistry from Northwestern University in 1983 and 1986, respectively.

TITANIUM DIOXIDE NANOTUBE COMPOSITES FOR PHOTOCATALYSIS

Kenneth J. Balkus, Jr.,

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Titanium dioxide nanotubes (TNT) have been prepared by hydrothermal synthesis and modified with quantum dots. The high surface area and aspect ratio of TNTs makes them attractive for applications in photocatalysis and photovoltaics. Coupling the TNTs with small band gap quantum dots might enhance the efficiency by utilizing more of the solar spectrum. For example, PbS quantum dots (PbS QDs) which absorb in the near IR were prepared on the inside and/or outside surfaces of TiO_2 nanotubes by using thiolactic acid as an organic linker. The sizes of PbS QDs were controlled by employing a dip coating process to anchor the PbS QDs onto the TiO_2 nanotubes. The PbS QDs with diameters of 2–10 nm were obtained by adjusting the concentration of thiolactic acid. TiO_2 nanotubes with PbS QDs located only inside the nanotubes were prepared by first coating the tubes with a cationic surfactant (see figure). The TNTs were shown to have exceptional photocatalytic properties for the degradation of organic dyes in comparison to Evonik Degussa's P25. The PbS quantum dots further enhance the catalytic activity and the TNT composites retain activity even when the light source is filtered to exclude below 600nm. The TNTs are insoluble but can also be solubilized by wrapping the nanotubes with various polymers such as polyarginate. This has created opportunities in biological areas such as in photodynamic therapy. For example, the QD modified TNTs have been shown to be effective antibacterial agents.



Ken Balkus is a Professor of Chemistry at UT Dallas, where most of the research in his lab involves nanoporous metal oxides like zeolites and related molecular sieves as well as inorganic-organic hybrid frameworks, as membranes, smart textiles, sensors, solar cells and fuel cells. He received his BS in 1982 (WPI) and PhD in 1986 (U. Florida), and did his post-doc at UPenn (1986-88). He is on the Editorial Board of Microporous Mesoporous Materials, and most recently, he received the 2008 ACS Doherty Award.



CATALYTIC ROUTES TOWARDS WELL-DEFINED POLY- α -PEPTOIDS

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Poly- α -peptoids with proteinogenic or synthetic side-chains at the nitrogen atoms are structural mimics of poly- α -peptides. Different from poly- α -peptides whose well-defined secondary structures are stabilized through hydrogen bonding interactions, poly- α -peptoids are largely free of hydrogen bonding. Yet their secondary structures can be controlled through the judicious design of the side-chains. They complement poly- α -peptides with regards to their secondary structure and conformational stability and are attractive building blocks for novel stimuli-responsive materials where the physical properties are coupled to the conformational transition of the polymers.

We will present our recent progress on developing catalytic polymerization methods for the controlled synthesis of poly- α -peptoids. The design of single-site metal catalysts and studies of their activities in mediating the polymerization of N-substituted carboxylanhydride ($^N\text{R-NCA}$) will be discussed. We have found that our nickel catalyst can mediate the polymerization of $^N\text{R-NCA}$ and it appeared to be more robust than conventional organic initiators when residual protic impurity present in the monomers.

Donghui Zhang is an assistant professor in the Chemistry Department of Louisiana State University. She obtained her Ph.D. in Organometallic Chemistry from Dartmouth College in 2003 and did one-year postdoctoral research at University of Minnesota on the synthesis and characterization of polymers from biorenewable source materials. She joined LSU in 2007 after a two-year stint as a research faculty in New Mexico State University. Her current research interests focus on polymer catalysis, design and synthesis of functional polymeric materials.

IMMOBILIZED CATALYSTS: NEW INSIGHTS BY SOLID-STATE NMR SPECTROSCOPY

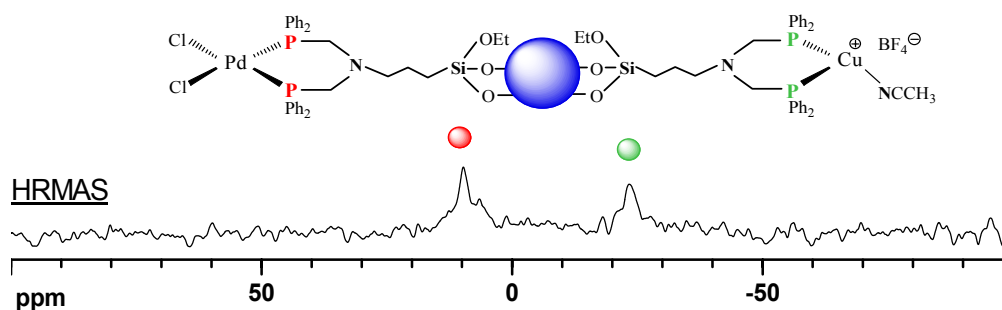
Janet Bluemel

Texas A&M University, Department of Chemistry, P.O. Box 30012 (mail stop 3255), College Station, TX 77842-3012; Tel.: (979)845-7749; FAX: -5629; e-mail: bluemel@tamu.edu

Molecular catalysts immobilized on oxide supports are easy to design, and they are as selective and active as their homogeneous analogues. Furthermore, they can easily be separated from the reaction mixture and recycled many times.¹ These features make immobilized catalysts attractive not only for academic, but also for industrial purposes. Homogeneous catalysts can be bound to oxide supports by phosphine linkers, as shown in the Figure below.^{2,3} Silica is the most favorable support, both from an analytical, and preparative point of view. For the analysis of the resulting amorphous solid materials we optimized classical solid-state and suspension NMR spectroscopy.^{4,5} Both can be employed for probing the nature and mobility of surface-bound species.

In the first part of my presentation, the HRMAS method, which we have implemented for immobilized catalysts, and the kind of information it provides, will briefly be described. This section should be of interest to all participants of the SWCS meeting, because our new technique can be applied to a wide variety of systems in chemistry and related disciplines.

Next, new insights concerning the syntheses, immobilization, characterization, activities, and lifetimes of mononuclear catalysts,¹ as well as intrinsic problems therewith will be discussed. New perspectives that have been obtained with the heterodimetallic Pd(0)/Cu(I) Sonogashira catalyst system using ³¹P HRMAS,² will be presented:



The most fascinating aspect of the Sonogashira catalyst system concerns the mobility of the Pd fragment on the surface, which can be found in case of sub-monolayer surface coverages by HRMAS NMR.

Finally, a new generation of successful linker systems will be presented, only one of which has been communicated so far.⁶ These new linkers finally solve two of the most persistent problems of immobilized catalysts, (a) destruction of the catalyst by contact with the reactive support surface, and (b) deactivation by dimerization or agglomeration with neighboring catalyst molecules.

References: 1. (a) J. Blümel, *Coord. Chem. Rev.* **2008**, 252, 2410; (b) C. Merckle, J. Blümel, *Topics Catal.* **2005**, 34, 5. 2. T. Posset, J. Blümel, *J. Am. Chem. Soc.* **2006**, 128, 8394. 3. M. Bogza, T. Oeser, J. Blümel, *J. Organomet. Chem.* **2005**, 690, 3383. 4. T. Posset, F. Rominger, J. Blümel, *Chem. Mater.* **2005**, 17, 586. 5. S. Brenna, T. Posset, J. Furrer, J. Blümel, *Chem. Eur. J.* **2006**, 12, 2880. 6. Y. Yang, B. Beele, J. Blümel, *J. Am. Chem. Soc.* **2008**, 130, 3771.

Janet Bluemel (with German Umlaut Blümel) obtained her chemistry diploma from the Technical University of Munich, Germany in 1986. After her Ph.D. in Inorganic Chemistry at TU Munich in 1989 she joined the group of Peter Vollhardt at UC Berkeley as a postdoc. In 1991 Janet returned to TU Munich as an assistant professor (Habilitation) in Inorganic Chemistry. She moved to University of Heidelberg in 1998 as an associate professor in Organic Chemistry, and joined TAMU as full professor in 2007.



LIQUID PHASE CATALYTIC CONVERSION OF CELLULOSIC BIOMASS TO BIOFUELS AND BIOBASED PRODUCTS

Z. Conrad Zhang¹, Yu Su², Heather Brown², Haibo Zhao³, John Holladay², Xiwen Huang⁴, Guosheng Li², Xiaodong Zhou², Jim Amonette², John Fulton²

1 KiOR Inc.

2 Pacific Northwest National Laboratory

3 Huntsman Chemicals

4 BASF

Cellulosic biomass offers the most abundant renewable feedstock for a sustainable future in the production of liquid fuels and chemical products. The ability to convert biomass for the large-scale production of biofuels and biobased chemicals depends critically on the development of effective low-temperature processes. Compared to petroleum feedstocks, cellulosic biomass is characterized by typically very high oxygen content. One promising biomass-derived platform chemical is 5-hydroxymethylfurfural (HMF), from the conversion of C₆ sugar component of cellulose. HMF has been shown to be a versatile platform chemical for the production of liquid fuels. The ability to synthesize HMF directly from raw natural cellulose would remove a major barrier toward the development of a sustainable HMF platform. We report a single-step catalytic process where cellulose as the feed is rapidly depolymerized and the resulting glucose is converted to HMF under mild conditions. 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) is a solvent that readily dissolves cellulose. A pair of metal chlorides containing CuCl₂ dissolved in the [EMIM]Cl solvent at a temperature range of 80-120°C collectively catalyze a single-step process, converting cellulose to HMF with an unrefined 96% purity among recoverable products (at 55.4 ±1.8% HMF yield). After extractive separation of HMF from the solvent, the catalytic performance of recovered [EMIM]Cl and the catalysts was maintained in repeated uses. Cellulose depolymerization occurs at a rate that is about one order of magnitude faster than conventional acid-catalyzed hydrolysis in aqueous system. In contrast, single-metal chlorides at the same total loading showed considerably less activity under similar conditions.

Conrad Zhang is the Director of Science and R&D, KiOR Inc., a Khosla Venture founded bio-energy Company, with a leading position in technology for the production of non-ethanol alternative fuels from biomass. He was previously at the Institute for Interfacial Catalysis at PNNL as Chief Scientist, and at companies like Akzo Nobel and Johnson Matthey, and at Northwestern University. He received his B.S. (1982) in Chemistry from Lanzhou University, China, and Ph.D. (1988) in Chemistry from University of Connecticut. He is a co-founder of the Catalysis Division at ACS, a Member of Advisory Board of the Algae Energy Research Center at UT Austin, and was Chairman of the Catalysis Society of Metropolitan New York, among other activities.



THE IMPORTANCE OF NANO-ARCHITECTURE IN HETEROGENEOUS CATALYSIS

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Department of Chemical & Biological Engineering
University of Wisconsin-Madison
Madison, WI 53718

Catalysis is at the heart of solutions for energy and environmental problems our society is facing today. Over the last few years, periodic self-consistent Density Functional Theory (DFT-GGA) calculations have emerged as a valuable partner to experiment in explaining reactivity of transition metal surfaces. In this talk, we will attempt to demonstrate how first-principles methods can extend beyond the detailed mechanistic analysis of catalytic reactions to reach the ambitious goal of identifying promising catalysts for specific applications. Among others, we will discuss opportunities to design bimetallic and ternary alloy catalysts for highly selective hydrogen transfer reactions, and for cheaper and more active oxygen reduction (ORR) catalysts, the latter being most relevant to the cathode reaction of low temperature fuel cells. Furthermore, through a combination of theory and experiments, we will demonstrate the remarkable catalytic Preferential Oxidation (PROX) of CO in the presence of H₂, as performed by core-shell bimetallic nanoparticles with precisely controlled atomic thickness for the core/shell.

Since 1999 Manos has been with the Department of Chemical & Biological Engineering, University of Wisconsin - Madison. He is one of the world leaders in the area of computational chemistry in catalysis. He has also served as Visiting Professor, Department of Chemical Engineering, Technical University of Denmark, Lyngby, Denmark. He received his Diploma in Chemical Engineering (1988) from NTUA (Greece), and MS (1989, 1993) and PhD (1994) in Chemical Engineering and Scientific Computing from U. Michigan. The primary research focus of Mavrikakis' group is the fundamental understanding of surface reactivity, using state-of-the-art first-principles methods, and extensively collaborating with experimental experts.

2009 Emmett Award Citation:

"For his elucidation of the fundamental aspects of the surface chemistry for well-established catalytic processes, and his leadership in the use of Density Functional Theory to set directions for future research in the search for new catalysts and new catalytic processes."



POSTER ABSTRACTS

1. CO Dissociation Induced by Adsorbed Oxygen and Water on Ir(111)

Ming Pan, Son Hoang, Jinlong Gong, and C. Buddie Mullins*
Department of Chemical Engineering, University of Texas at Austin
1 University Station C0400, Austin, Texas 78712-0231

In this poster, the oxygen-water interaction and the dissociation of CO have been studied on the Ir(111) single crystal surface under ultra high vacuum (UHV) conditions. With the aid of isotopically labeled reactants and temperature programmed desorption (TPD) measurements, we have found a strong interaction between adsorbed atomic oxygen [dioxygen can dissociatively chemisorb on Ir(111)] and water on Ir(111). When H_2^{18}O and $^{16}\text{O}_a$ were co-adsorbed on Ir(111), the TPD spectra showed the production of H_2^{16}O , $^{16}\text{O}^{18}\text{O}$, and $^{18}\text{O}_2$, as well as the occurrence of a new desorption feature at 235 K (water molecularly desorbs at 175 K and 150 K) indicating dissociation of water in which adsorbed hydroxyl groups ($\cdot\text{OH}$) are likely intermediates. We have also investigated CO dissociation on Ir(111) in the presence of oxygen and water. Although CO dissociation has not been observed on clean Ir(111), we noticed that co-adsorbed atomic oxygen induced and enhanced CO dissociation [e.g. $^{13}\text{C}^{16}\text{O}$ was detected desorbing from $^{13}\text{C}^{18}\text{O}$ and ^{16}O co-adsorbed on Ir(111)]. Similar phenomenon was observed on CO covered Ir(111) when water and oxygen were co-adsorbed (solely adsorbed water did not induce dissociation of CO), likely indicative of the importance of formed hydroxyl groups.

2. Selective Oxidation of 2-butanol on Oxygen-Precovered Au(111)

Ting Yan, Jinlong Gong, C. Buddie Mullins

We report on the selective oxidation of 2-butanol on oxygen pre-covered Au(111) under ultra-high vacuum conditions employing temperature programmed desorption (TPD) and molecular beam reactive scattering (MBRS). The 2-butanol adsorbs and desorbs molecularly on the clean Au(111) surface. However, the oxygen pre-covered Au(111) surface can promote the reaction of 2-butanol into 2-butanone with high selectivity at low oxygen coverages. The C-O bond cleavage in 2-butanol is found in experiments with isotopically labeled $^{18}\text{O}_a$. Full oxidation and dehydration are also activated. Two surface intermediates are proposed for the selective oxidation of 2-butanol: 2-butoxide and η^2 -aldehyde.



3. Characterization of Alloy Electrocatalysts by Combined Low-Energy Ion Scattering Spectroscopy and Electrochemistry

Stephanus Axnanda & Dr. D. W. Goodman
Texas A&M University, Chemistry Department

Pt-Co bimetallic model catalysts were prepared as thin film alloy on single crystal and HOPG substrate. The surface composition and morphology were characterized with low energy ion scattering spectroscopy (LEISS), x-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), and Temperature Programmed Desorption (TPD). Electrocatalytic activity towards oxygen reduction reaction (ORR) and functional stability were characterized via cyclic voltammetry (CV). The main goal in this study is to define the surface phase diagram of Pt-Co alloys, i.e. the surface versus bulk concentration of Pt or Co. This surface phase diagram will show how the amount of Pt and Co on the surface varies from the bulk as the amount of one metal is increased over the other. Relative to the bulk, the surface of the alloy system is enriched in Pt. A second goal of this study is to combine electrochemical measurements on the Pt-Co model alloys with surface characterization techniques. The electrocatalytic activity of different compositions of Pt and Co will be determined. Additionally, stability of prepared films will be tested by holding at selected standard operating voltages. Changes in Pt-Co surface composition after each electrochemistry experiment will be determined by observing the surface composition using LEISS and XPS. The dissolution of alloying metal, Co, and the effect of particle size on the surface phase diagram and the catalytic activity of Pt-Co towards ORR will also be discussed.



4. Dynamics of Diesel Particulate Filter Regeneration

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Department of Chemical and Biomolecular Engineering,
University of Houston, Houston, Texas, USA, 77204

The spatiotemporal combustion of soot on a single layer planar diesel particulate filter (DPF) was followed by the Infra-red imaging. The experiments revealed some rather surprising novel features about the evolution and dynamics of the soot combustion. The combustion rate was uniform all over the surface at low oxygen concentration and a feed temperature of 635°C. At higher oxygen concentration the soot combustion was initiated at either one or several locations and the hot zone, bounded by steep temperature fronts propagated along the surface. The maximum temperature of the moving fronts exceeded by 100 °C those obtained during the uniform combustion. The peak temperature and velocity varied as the temperature fronts propagated on the surface. As the flow rate per unit filter surface area was increased, the ignition location shifted from the entrance to the exit of the DPF for a soot loading of 10 g/L. A transient temperature rise a sudden decrease of the inlet gas temperature by 100 °C led to a transient temperature rise. This behavior is similar to the wrong-way behavior in a packed-bed reactor. Thus, a rapid shift of a diesel car driving mode from drive fast to idle may lead to a large transient temperature rise, much higher than those, encountered under either the original or final operating conditions. Such transient temperature rise may explain the failure of a DPF material integrity during uncontrolled regeneration.

5. CO Oxidation over Pd-Au alloy at near-atmospheric pressures: the critical role of contiguous Pd atoms

Feng Gao, Yilin Wang, Yun Cai, and D. Wayne Goodman^{*}
Texas A&M University; Department of Chemistry
P.O. Box 30012, College Station TX 77842-3012, USA

The surface of a Pd-Au alloy has three different surface sites, i.e., Au sites, isolated Pd sites and contiguous Pd sites. Binding energies of CO on these sites can be obtained isothermally using infrared reflection absorption spectroscopy (IRAS). It is demonstrated that gas-phase CO pressure higher than ~0.1 Torr is required to segregate sufficient amount of Pd to the surface of a well-annealed AuPd(100) sample to form contiguous Pd sites. These contiguous sites are critical in dissociating O₂ for low-temperature CO oxidation. Measured reaction kinetics demonstrates that when these sites are not available, there is no CO oxidation reaction occurring whereas higher reaction rate is achieved on a surface with higher coverages of contiguous Pd sites.



6. Growth and Characterization of High Surface Area Titanium Carbide.

David W. Flaherty, R. Alan May, Domingo Ferrer, Keith Stevenson, C. Buddie Mullins
Departments of Chemical Engineering and Chemistry, 1 University Station, CO400
University of Texas at Austin, Austin, Texas, 78712

High surface area, porous titanium carbide films have been synthesized employing physical vapor deposition of titanium at glancing angles under high vacuum within an ethylene ambient. The composition, surface area, and morphology of the TiC films were studied as a function of deposition conditions including ethylene pressure, titanium deposition angle, substrate temperature during growth and post-deposition annealing temperature. At high or glancing deposition angles ($\sim 80^\circ$ - 85°) synthesis produces films composed of arrays of porous nanocolumns of TiC while deposition at more moderate angles, less than 70° , results in continuous, reticulated films. The maximum specific surface area ($840 \text{ m}^2/\text{gram}$) is obtained by growth with an incident titanium deposition angle of 65° , an ethylene pressure of 1.5×10^{-7} Torr, and a substrate growth temperature of $\sim 350 \text{ K}$. This result is in contrast to previous investigations using related physical vapor deposition techniques which have generally shown that films with the greatest porosity and surface area are grown by deposition at cryogenic temperatures ($T \leq 77 \text{ K}$). The fact that the surface area is maximized at this uncharacteristically high growth temperature implies that thermally induced decomposition of ethylene and the subsequent desorption of reaction byproducts are important steps for the synthesis of these materials. Deposition of TiC at 350 K not only results in high specific surface areas, electron diffraction measurements indicate that these films are polycrystalline. Titanium carbide films created in this study are thermally robust and resistant to sintering, retaining greater than 70% of their initial surface area after annealing to 1000 K . The ability to deposit TiC near room-temperature should allow these films to be deposited onto a wide variety of substrates.



7. Synthesis and Characterization of Ge-Al-ZSM-5 Made in Alkaline Media

Anirban Ghosh, Nataly Garcia Vargas, Scott F. Mitchell, Scott Stevenson and Daniel F. Shantz*.

**Correspondence: Daniel F. Shantz.*

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The synthesis and characterization of a series of Ge-Al-ZSM-5 samples made in hydroxide media is reported. From the work reported, several interesting and significant conclusions can be ascertained about MFI zeolites crystallized in the presence of multiple heteroatoms. X-ray fluorescence (XRF) and X-ray photoelectron spectroscopy (XPS) indicate that there is a germanium rich overlayer on these crystals. Electron microscopy results validate this conclusion, and also indicate that the aluminum distribution through the samples is uniform. While the powder X-ray diffraction data does not reveal the presence of an impurity, the nitrogen adsorption data shows a reduced nitrogen uptake before the surface germanate material is removed. The crystal size and the germanium uptake appear to correlate strongly with pH, as lower pH values lead to higher germanium uptake and larger crystal size. X-ray absorption spectroscopy results indicate that the germanium is tetrahedrally coordinated in the zeolite framework, and that GeO_2 is not present in these samples after they have been ion exchanged with sodium nitrate solutions. This work highlights some of the complexities involved in characterizing zeolite crystals with multiple heteroatoms and verifying that the materials are in fact phase pure.



8. Nature of Transitioning Alumina and Silver Interactions on Supported Silver Catalysts for SCR

Morgan Reed¹, Andrew Gomes^{1,2}, Dan Rutman^{1,2}, David Cocke^{1,3}

¹ Department of Chemical Engineering, Lamar University, Beaumont, Texas

² Materials Instrumentation Center, Lamar University, Beaumont, Texas

³ Gill Chair of Chemical Engineering, Beaumont, Texas

Selective removal of NO_x from combustion processes by catalytic reduction using hydrocarbons or other reductants has attracted great interest from both university and industrial researchers. There are two main groups of promising catalysts: the zeolite-based catalysts such as Cu/ZSM-5 and the alumina based catalysts such as Ag/Al₂O₃. In the latter catalyst system, the role of the alumina support and the nature of the silver species and their interaction are in question. Factors of increasing importance are: the surface concentration of silver, the kind of silver species (Ag⁰ clusters, Ag⁺ ions fixed to the support surface or involved in an Ag aluminate phase), formation of bulk Ag₂O, and the acid-base surface characteristics of the support. The role of all parameters is not yet fully understood due to the complexity of the catalyst/reaction system. In this work, we are using analytical scanning electron microscopy, SEM, X-ray Diffraction, XRD, thermal analysis (thermal gravimetry (TG) and differential scanning calorimetry, DSC), and a Hiden CATLAB to explore the Ag/Al₂O₃ catalysts with 2.5% Ag content. The effect of the phase changes in the transitional alumina has been tracked and insight into its influence on the nature of the active silver species and the nature of the support has been delineated.

9. Particle Size Distribution and Dispersion Stability of Cloisite Clay Using a Bench Top Dispersion Analyzer the LUMiSizer[®]

Morgan Reed¹, Gary Beall², and David L. Cocke^{1,3}

¹ Department of Chemical Engineering, Lamar University, Beaumont, Texas

² Department of Chemistry, Texas State University, San Marcos, Texas

³ Gill Chair of Chemical Engineering, Lamar University, Beaumont, Texas

The particle size distribution and dispersion analysis of suspensions of natural montmorillonite was determined by a dispersion analyzer utilizing extinction and transmission profiles. Dispersion Analyzers provide a useful tool for the characterization and optimization of suspensions of particles ranging from the 0.1 micron range all the way to hundreds of microns. The present work reports on the determination of the particle size distribution using space and time extinction profiles. The particle size distribution is obtained by one of the following two methods; examining the variation of the transmission profiles at a fixed position of the sample over the entire centrifugation time or by analyzing the extinction variation over the entire sample length for any specific centrifugation time interval. The advantage of the latter method is the potential to reduce the time of measurement considerably.



10. Heterogeneous catalysts used to prepare Biodiesel

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Nowadays the main energy source used is the petroleum based, however, the progressive exhaustion of its reserves is a global reality [1]. Hence, many studies suggest the use of other energy sources and they are preferably renewable and environmentally benign. In this context vegetable oils appear as an alternative to mineral diesel oil (Li and Xie, 2006). A biofuel derived from vegetables oils is biodiesel that is industrially prepared using a vegetable oil, methanol and catalyst (NaOH, KOH or MeONa). However these catalysts provide some problems during the process like, emulsion, soap, and the separation process is difficulty. So, we have prepared some heterogeneous catalysts to use in the transesterification reaction to obtained biodiesel. The first generation of catalyst was prepared using chitosan and Co^{+2} and Cu^{+2} (CCo and CCu), and then they were used in the transesterification reaction of babassu and soy bean oils. In this case methanol was used as the alcohol. The conversion in biodiesel was: Soy bean Biodiesel - CCo (94.01%), Soy bean biodiesel - CCu (88.82 %), Babassu biodiesel -CCo (86.65 %), and Babassu Biodiesel - CCu (71.89 %). The second generation of catalysts to obtained biodiesel was $\text{CuO}/\text{Al}_2\text{O}_3$, $\text{CoO}/\text{Al}_2\text{O}_3$, and $\text{MnO}/\text{Al}_2\text{O}_3$. The catalysts were prepared by the method of co-precipitation and they were calcined into two temperatures: 400 °C and 650 °C. The conditions for transesterification reaction from babassu oil using the heterogeneous catalysts were evaluated, and the best parameters were: 6:1 (molar ratio oil/methanol) and 24 h. The optimum condition was applied to all biodiesel obtained using the catalysts (CuO400), (CoO400), and (MnO400) with yields of 66.70, 98.23, and 68.10, and for biodiesels transesterified twice obtained with the catalysts (CuO650), (CoO650), and (MnO650) with yields of 83.67, 97.86, and 94.13%. The use of heterogeneous catalysts was very satisfactory with respect to conversion of methyl esters (biodiesel).

[1] Abreu, F.R., Alves, M.B., Macedo, C.C.S., Zara, L.F., Suarez, P.A.Z., 2005, J. Mol. Catal. A: Chemical, 227 (1-2), 263-267.

[2] Li, H., Xie, W., 2006. Catal. Lett., 107 (1-2), 25-30.



11. Controlled conversion and product selectivity in the Nitroaldol reaction by Ordered Mesoporous Silica (OMS)-amine Nanocomposites

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Several amine-OMS materials were evaluated as catalysts for the Nitroaldol reaction. The results indicated that primary amine groups favors the synthesis of nitrostyrene (i.e the alkene product), while the secondary amine groups result in the high yield of nitroalcohol product. The secondary amine groups with different spatial structures, such as simple methylpropylamine, benzylpropylamine, piperazine groups, displayed different amine-silanol bifunctionality that influences the extent of nitrostyrene formation in the nitroaldol reaction. The hydrophobicity and the pore size also influence the catalytic process.

Dendrons attached to OMS were also investigated as catalysts for this reaction. The dendritic structure extends the spatial arrangement of organoamine groups, controls the density, and potential site isolation of the functional groups on the OMS surface. The high conversion in the nitroaldol reaction and the clear selectivity to nitroalcohol product indicates that the steric conditions of the functional amine groups on OMS influences their catalytic properties.

12. Transition metals an the catalysis of SWNT growth

Alvin Orbaek, Christopher Crouse, Andrew R Barron.

The catalytic growth of single walled carbon nanotubes was accomplished using bi-metallic nanoparticles. Inverse spinel ferrite nanoparticles of iron series transition metals Co, Mn, Fe, Ni, and Cu, of varying stoichiometry were found to affect growth. Critical density of the particles across the substrate allowed for vertically aligned growth to be achieved. The VA-SWNTs could be analyzed using ensemble techniques such as SEM and Raman. Observed differences of SWNT characteristics such as diameter, length, and purity, has led to a qualitative understanding about how these metals affect growth.



13. Surface atomic distribution and water/atomic oxygen adsorption on Pt-Co alloys

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Pt-based alloy surfaces are used to catalyze the molecular oxygen and its subsequent reduction to water on fuel cell electrodes. Due to surface segregation phenomena, alloy surface composition may be very different from the overall composition. Also, the adsorption of intermediates or products species on the surface may modify the properties of both surfaces and species. Here we address the problem of determining surface atomic distribution using density functional theory (DFT) calculations on slabs of PtCo and Pt₃Co overall compositions, as well as a water molecule adsorption on PtCo(111) and Pt-skin structures. Pt-rich surfaces are energetically favored under vacuum in the PtCo and Pt₃Co alloys. The adsorption trend on the studied structures agrees with the d band model, with stronger adsorption at higher surface Co composition. The bonding between water and surfaces of PtCo and Pt-skin monolayers are investigated in term of energetic, electron orbitals and electron densities. We also found that water adsorption on Pt-skin shows larger effect on atomic oxygen binding energy than that on PtCo. On both surfaces, the surface reconstruction occurs at high oxygen coverage (~0.5 ML) but the presence of water at low oxygen coverage of 0.125 ML can present a comparable magnitude of surface reconstruction.



14. Characterization and Elevated Pressure Reactivity of Rh/SiO₂ Model Catalyst Surfaces

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Model catalyst surfaces, consisting of metal particles supported on a planar oxide support, hold the potential to help bridge the material gap between single crystal and technical catalyst studies. However, work remains to understand the catalytic properties of such model surfaces under elevated pressure conditions (~1 atm). For example, determining the extent of quantitative and qualitative agreement of activity and selectivity of model catalyst systems and single crystal surfaces for well characterized reaction systems (e.g. CO+O₂) requires additional investigation. Here, we discuss recent work characterizing reaction kinetics on Rh/SiO₂ model catalyst surfaces, prepared in-situ in a contiguous high pressure reactor-UHV surface analysis system. STM and TPD are employed to assess nano-particle size, surface sites and binding sites as a function of metal coverage. Elevated pressure reaction kinetics are studied employing two probe reactions: (a) structure-*insensitive* CO oxidation reaction (CO+O₂) and (b) structure-*sensitive* alkane (C₄H₁₀+H₂) hydrogenolysis reaction. The experimental setup allows for complementary studies on single crystal surfaces (Rh(111)) under identical reaction conditions in the same reactor, for direct comparison. Results illustrate that model catalyst surfaces provide a useful vehicle for qualitative and quantitative study of reaction kinetics under elevated pressures approaching those of a working catalyst.

15. MECHANISTIC STUDIES OF THE COUPLING REACTION OF OXETANE AND CO₂ TO AFFORD POLYCARBONATES CATALYZED BY CHROMIUM SALEN COMPLEXES.

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Chromium(III) salen derivatives in the presence of an azide ion initiator have been shown to be very effective catalysts for the coupling of oxetane and carbon dioxide to provide the corresponding polycarbonate with minimal amount of ether linkages. The mechanism of the coupling of oxetane and carbon dioxide has been studied by *in situ* infrared and ¹H NMR spectroscopy. The formation of copolymer is shown to proceed by two routes, by the intermediacy formation of trimethylene carbonate (TMC), which was observed as a minor product of the coupling reaction, and by the direct enchainment of oxetane and CO₂. Efforts at tuning the selectivity of the oxetane and CO₂ coupling process for cyclic carbonate or copolymer formation have been directed by altering the



anionic initiator. Anion initiators that are good leaving groups, e.g., bromide and iodide are most effective at affording TMC, and hence more copolymer is formed by the ring-opening polymerization of preformed TMC.

16. Adsorption and absorption of Carbon in $L1_2\text{-Fe}_3\text{Al}$ (111) surfaces

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The adsorption, absorption and diffusion of carbon atoms in $L1_2\text{-Fe}_3\text{Al}$ (111) surface is studied using density functional theory. In the adsorption and absorption study it is found that carbon atoms prefer to locate in positions characterized by strong bond energies between carbon and iron atoms; in addition, surface reconstruction is observed when carbon atoms are in certain locations. At high concentration of carbon on the surface, the formation of carbon structures such as graphite is observed. Carbon diffusion from the surface to the subsurface is studied; it is found that the increase of carbon surface coverage induces lattice deformation that facilitates carbon penetration.

17. Formation of carbon nanostructures on stepped metal surfaces

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We present a density functional theory study of carbon adsorption and absorption on stepped transition metal surfaces, using the projector-augmented wave method and the Perdew-Burke-Ernzerhof exchange-correlation functional, within the generalized gradient approximation. We discuss a series of interesting carbon structures formed over the (211) Co surface which evolve as the C concentration on the surface increases. At low concentration of C we observe the formation of zig-zag chains where each of the atoms in the zigzag are alternatively bonded to a step and to a terrace site. After more carbon is added to the system, perfect graphene structures are formed. Interestingly, our findings are in excellent agreement to recently published experimental results. We also extend the study using chiral surfaces, to analyze if carbon atmospheres on chiral Co surfaces may also lead to the formation of alternative structures. Preliminary calculations suggest that horizontally aligned nanotubes could be also the result of surface patterning.



18. Theoretical study of the interactions of 1,3,5-hexahydro-1,3,5-trinitro-1,3,5-triazine and an aluminum surface.

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Security at airports and public places has gained concern among authorities. Thus, implementing quick, safe and reliable methods of detecting explosives has become crucial. Although at present, there are a variety of methods to accomplish this task, they have not been totally effective in identifying specific chemical substances. Terahertz spectroscopy that appears as a promising technique to complement tools for explosives detection, requires a careful understanding of molecule/environment interactions, including surfaces where substances may be attached.

Here we analyze a typical compound: 1,3,5-hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), being one among several nitramine compounds used as energetic materials. Taking α -RDX as a model we have simulated spectra of its dimer in gas phase. Calculations using rb3lyp/6-311g(d,p) and hf/6-311g(d,p) chemistry models help us to understand RDX chemical behavior, and account for basic intermolecular interactions that are the first step for the elucidation of more complex solid-state modes.

We also discuss the interaction between RDX and a model surface of sixteen aluminum atoms and its corresponding THz spectra. We analyze several THz bands corresponding to intermolecular, RDX-aluminum, and aluminum-aluminum interactions and also some bands assigned to methyl groups rotation. We compare the simulated and experimental spectra in order to assign THz experimental bands to intermolecular interactions.

19. Size Effect on the Stability of Cu-Ag Nanoalloys

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Bimetallic nanoclusters are of great interest in applications ranging from catalytic to optic and electronic applications. In these solid nanoparticles, the mixed state may be in either single (random) or two-phase state (core-shell or other ordered configuration); for instance, Cu-Ag nanoalloys are usually found in core-shell structures, due to segregation of Ag toward the alloy surface. Properties of Cu-Ag nanoalloys are expected to make this a suitable catalyst for processes such as the synthesis of methyl glycolate and selective oxidation of ammonia. However, in order to design and synthesize efficient nanocatalysts, a better understanding has to be achieved of the stabilities of core-shell and random configurations for this nanoalloy. In this work, we



use classical molecular dynamics (MD) simulations to study the phase stability of Cu-Ag nanoalloys through the analysis of the Gibbs free energy of mixing (ΔG_{mix}) for both random and core-shell clusters, as functions of nanoparticle size, temperature and composition. The configuration with the more negative ΔG_{mix} is considered more stable and would be the preferred of the system. Results of MD simulations indicate that in most cases studied Cu-Ag systems prefer core-shell configurations.

20. Surface chemistry of 2-propanol on clean and O-pre-covered Ir(111).

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The decomposition and oxidation of 2-propanol on clean and O-pre-covered Ir(111) were studied using temperature-programmed desorption (TPD) and molecular beam reactive scattering (MBRS). 2-Propanol reacts via a 2-propoxide intermediate, followed by β -hydride elimination (the reaction limiting step), is the main reaction pathway, producing acetone at 225 K and adsorbed hydrogen. Reactive scattering measurements show that on clean Ir(111), at high temperature (600 K), 2-propanol reacts mainly via non-selectively decomposition, producing CO, H₂ and adsorbed carbon. No acetone production was observed when 2-propanol was impinged the sample at 600 K. On O-covered Ir(111) surface, the acetone desorption peak shifts to lower temperature with increasing pre-coverage of O. Interestingly, acetone is still formed upon impinging a 2-propanol beam to O-Ir(111) at 600 K. Further investigation is still ongoing to clarify the role of pre-covered O on the oxidation of 2-propanol on the Ir(111) surface.

21. Fischer-Tropsch synthesis on a Co/SiO₂ model catalyst.

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Supported cobalt catalysts have been extensively studied for Fischer-Tropsch synthesis (FTS) because of their higher activity compared to commercially used iron catalysts. In this study, a Co/SiO₂ model catalyst was prepared by depositing metallic cobalt onto silica films in ultrahigh vacuum conditions. Fischer-Tropsch synthesis was carried out on this catalyst at a total pressure of carbon monoxide and hydrogen between 250 and 760 Torr. The effects of reaction temperature and pressure on kinetics and chain growth probability were investigated. The turnover frequency, activation energy, and product distributions were found in good agreement with those obtained on cobalt-based technical catalysts. The catalyst surfaces were studied by X-ray photoelectron spectroscopy after FTS reactions. It was found that the catalyst deactivation was



mainly caused by carbonaceous depositions, whereas the formation of cobalt oxide or cobalt carbide was not observed after reactions.

22. Platinum-Silica Model Catalysts at Elevated Pressures

M. Lundwall, S.M. McClure, Z. Zhou, D.W. Goodman

Well-defined model catalysts offer information that is difficult to ascertain on complex industrial catalysts particularly with respect to surface analysis and size effects. Here, we prepare Pt/SiO₂ model catalysts on a Mo(112) single crystal in ultra high vacuum and characterize the samples with AES, IRAS, TPD, and STM. Chemisorption experiments reveal step-site characteristics in qualitative agreement with what has been observed on stepped Pt single crystals. The model catalyst samples are subsequently transferred *in-situ* to a contiguous high pressure cell where reactions are performed. First, CO oxidation reactions are performed under CO dominant conditions to elucidate active site estimates under elevated pressures. We demonstrate this method to be an excellent means to extract site estimates under elevated pressures. Second, after obtaining site estimates from CO oxidation, we perform alkane hydrogenolysis reactions at elevated pressures (≈ 250 torr) in the same apparatus and monitor changes in activity and selectivity (Pt particle sizes ranging from 1-6nm) with a GC. Our results are compared and referenced to a platinum single crystal which has been run in the same apparatus under identical conditions. The implication of this research is three-fold: bridging the materials gap between model and technical surfaces, providing a unique method for estimating surface active-sites, and demonstrating the differences between structure *sensitive* and *insensitive* behavior on solid-state Pt-catalysts.

23. Study of Cobalt-Rhenium based catalysts for conversion of syngas to oxygenates

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Ethanol derived from syngas is a potential source of this oxygenate, which can be used as energy carrier or fuel additive. Selecting a suitable catalyst for the conversion of syngas to oxygenates, particularly C₂-oxygenates has been well-studied. Rhodium-based catalysts have consistently shown the highest selectivity for C₂-oxygenates. However, the high cost of rhodium has led to efforts to develop catalysts based on less costly metals.

There are several non-rhodium based catalysts which are active for the synthesis of C₂-oxygenates. They are mainly based on Co-Cu [1,2], modified Fischer-Tropsch catalysts of Iron [3-7], cobalt [8,9] and Ru [10,11] and modified nickel-methanation catalysts [12]. Silica supported cobalt catalysts modified by rhenium and zirconium have been found to be active for the synthesis of C₂-oxygenates in the work reported here. The catalysts

were synthesized by co-impregnation. Si support was modified by 2%Zr before the cobalt impregnation. The precursors used for the synthesis were cobalt nitrate and cobalt acetate. One of the catalysts was modified by adding 1% Mn. The catalysts were characterized by TPR, XRD and BET surface area. The experiments were performed with synthesis gas ($\text{CO}:\text{H}_2 = 1:2$) at 10 bar pressure and the temperature was varied from 230°C to 300°C. The catalyst was reduced at 400°C for 2 hours before carrying out the reaction.

The precursor was found to have a significant effect on the conversion of syngas (CO and H_2) to oxygenates. The acetate precursor was found to be more active and selective for ethanol as compared to the nitrate precursors. Also the Mn promotion was found to increase selectivity towards ethanol.

Further work will include study of the mechanism, e.g., to identify the surface abundant species at the reaction conditions. This will give an insight into the bond breaking and formation on the catalyst surface with varying reaction conditions—particularly the formation of the initial C-C bond.

- 1 A. Sugier and E. Freund, US patent, 4122110 (1978)
- 2 P. Courty et. al., J. Mol. Catal., 17 (1981) 241
- 3 W. Wenzel, Angew. Chem., B20 (1948) 225
- 4 R.B. Anderson et. al., Ind. Eng. Chem., 44 (1952) 391
- 5 H. Uchida et. al., Kogyo Kagaku Zasshi, (1953) 487
- 6 A. Razzaghi et. al., Appl. Catal., 13 (1984) 193
- 7 A. Pijiot and V. Perrichon, Appl. Catal., 13 (1985) 321
- 8 K. Fujimoto and T. Oba, Appl. Catal., 13 (1985) 289
- 9 F.N. Lin and F. Pennella, "Catalytic Conversion of synthesis gas and alcohols to chemicals" ed. By R.G. Herman, p.53, Plenum Press, New York, 1984
- 10 M. Inoue et. al., Appl. Catal., 11 (1984) 103
- 11 H. Hamada et. al., Chem. Lett., (1984) 1611
- 12 S. Uchida et. al., Shokubai (Catalysis), 26 (1984) 134



24. Relating Pentane Isomerization Activity to the Acidic Properties of WO_x/ZrO_2

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Acid metal oxide catalysts received enormous attention by a great percentage of the industrial and academic community in the last decade. Tungstated zirconia (WO_x/ZrO_2) is one of the most important metal oxide representatives and an excellent dehydration, acylation and isomerization catalyst. Its regeneration ability and structural stability drove a number of distinguished groups to investigate this challenging system resulting to complementary or conflicting fundamental models.

Most recently, the discrimination of Raman detectible WO_3 nanocrystals (1 – 4 nm) resulted to a novel model that associated maximum methanol dehydration activity to highest concentration of these nanocrystals. The direct or indirect effect of these nanospecies on the Lewis and/or Brønsted acidity of WO_x/ZrO_2 has not been established yet.

In this study, WO_x/ZrO_2 was synthesized using amorphous $ZrO_x(OH)_{4-2x}$ and crystalline ZrO_2 support precursors and characterized by nitrogen physisorption, x-ray diffraction and pyridine FTIR. Amorphous $ZrO_x(OH)_{4-2x}$ led to WO_x/ZrO_2 (WZrOH) that exhibited maximum isomerization activity at ~ 5.2 W-atoms \cdot nm⁻¹, and the crystalline ZrO_2 led to a material (WZrO₂) nearly inactive at all surface densities. Increasing the calcination temperature from 773 K to 973 K increased WZrOH activity and decreased total acidity due to the formation of WO_3 nanocrystals. Pyridine FTIR experiments have shown that maximum activity is not correlated to the *ex situ* Lewis and Brønsted properties of WO_x/ZrO_2 .



25. The Nature of the Union Carbide Catalyst (Chromocene/Silica): A Paramagnetic Solid-State NMR Study

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Immobilized chromium species represent one of the most important groups of catalysts for olefin polymerizations. In contrast to catalysts tethered to a support by linkers, 1-3 the Union Carbide (UC) Catalyst, can be generated by the direct reaction of chromocene with silica.⁴ The UC catalyst is highly active, and allows the polymerization without additives or pre-activation at ambient pressure and moderate temperatures. In this presentation we will demonstrate by paramagnetic solid-state NMR⁴ that the UC catalyst is composed of several mono- and dinuclear chromium surface species. Depending on the immobilization conditions the one or other product is favored. The most active species for polymerization is a mononuclear surface-bound Cr(III) half sandwich complex, which "ages" with time even prior to catalysis, forming dimers. All these results are supported by the synthesis of suitable mono- and dinuclear model compounds.

References

(1) J. Blümel, *Coord. Chem. Rev.* **2008**, 252, 2410. (2) Y. Yang, B. Beele, J. Blümel, *J. Am. Chem. Soc.* **2008**, 130, 3771. (3) T. Posset, J. Blümel, *J. Am. Chem. Soc.* **2006**, 128, 8394. (4) (a) M. Schnellbach, J. Blümel, F. H. Köhler, *J. Organomet. Chem.* **1996**, 520, 227. (b) J. Blümel, W. Hiller, M. Herker, F. H. Köhler, *Organometallics* **1996**, 15, 3474.

26. In-situ EXAFS Measurements of Pt DENs during CO stripping.

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The dendrimer-encapsulation technique is used to synthesize highly monodisperse Pt nanoparticles (1.8 +/- 0.4 nm). These DENs were immobilized onto carbon paper and studied electrochemically during CO adsorption and stripping. In addition, extended x-ray absorbance-fine structure (EXAFS) measurements were taken during each step of the catalysis. The in-situ EXAFS analysis demonstrates irreversible and reversible changes in the structure of the nanoparticle, including a limit on particle growth likely due to the dendrimer.



27. Using Gold to Enhance Palladium Catalytic Activity for Trichloroethene Reductive Dechlorination

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Trichloroethene (TCE) is one of the most common hazardous organic contaminants found in groundwater. This chlorinated solvent has been widely used in various fields including electronics manufacturing, metal degreasing, dry cleaning and chemical intermediates; therefore, lots of TCE has entered the environment through leakage, disposal and other pathways. TCE has been linked to liver damage, impaired pregnancies, and cancers in humans. Compared to conventional physical displacement methods such as air-stripping and carbon adsorption, remediation through the catalytic reductive dechlorination of TCE molecules is a more effective and desirable approach. In our previous work, palladium-on-gold colloidal nanoparticles (Pd/Au NPs, 4 nm) have been shown to catalyze the TCE hydrodechlorination (TCE HDC) reaction in water, at room temperature, and in the presence of hydrogen, with the most active Pd/Au NPs ($k = 1900 \text{ L/g}_{\text{Pd}}/\text{min}$) found to be >70 times more active than conventional mono-metallic Pd supported on alumina ($k = 26 \text{ L/g}_{\text{Pd}}/\text{min}$) on a per-Pd atom basis. Of note, our Pd/Au NPs exhibited volcano-like catalytic activity with different surface coverage. We proposed that Au enhances Pd activity through electronic and/or geometric effect.

In this poster presentation, we will address nanostructure evidence of our Pd/Au NPs to correlate it with reaction activity profile. We believe that geometric effect is the dominant effect for Au enhancement. The bimetallic Pd-on-Au nanostructure was determined by extend X-ray absorption fine structure (EXAFS) spectroscopy. The results showed that our Pd/Au NPs had Au-core and Pd-shell and most of surface Pd atoms were metallic. Pd atoms on Au NP surfaces exhibited better stability of zero oxidation state (metallic form) than pure Pd NPs which showed higher tendency to be oxidized. Kinetic analysis of TCE HDC reaction with Pd/Au NPs and Pd NPs will also be presented. This analysis verified a proposed reaction mechanism, and revealed information about the nature of active sites of different catalysts (Pd/Au NPs and Pd NPs).



A Brief History of the Southwest Catalysis Society

As recounted by Joe W. Hightower, Professor Emeritus, Rice University (April 2009)
B.S. '59 - Harding University; M.S. '61 and Ph.D. '63 - The Johns Hopkins University

I came to Rice University from the Mellon Institute in Pittsburgh during the summer of 1967 and immediately set out to meet catalyst people in the area. We announced an organizational meeting to be held at Rice, **Fall 1967**. There were 63 people as charter members of what was to become the Southwest Catalysis Club. Jim Richardson (Esso Research and Engineering, now University of Houston) drafted the Bylaws and was elected Vice President, Jack Lunsford (Texas A&M University) was Secretary, Paul Conn (Shell Oil) was the Treasurer, and I served as the first elected President. The officers held the first all-day Spring Symposium in May 1968 in the Grand Hall at Rice, and the SWCS was off and running (42 years and counting!). [As a note, I did my PhD thesis research with **Professor Paul Emmett** at Johns Hopkins, which involved isotopic tracer studies of secondary reactions that occur during catalytic cracking of petroleum products.]

At the time we started, there were about half a dozen "Catalysis Clubs" scattered around the country: Chicago, Pittsburgh, New York, Philadelphia, California, and perhaps one more. I knew people in all these "Clubs" though groups like the Gordon Research Conferences on Catalysis, and they all encouraged us to start a club in the SW. **Why 5 states?** Texas was obvious. Arkansas was included because of Sam Siegel (Chemist at UArk); Louisiana, because of several researchers at Esso in Baton Rouge; Oklahoma, because of several Phillips researchers in Bartlesville; and New Mexico, because of people at University of New Mexico and at Sandia National Labs in Albuquerque. In spite of the long distances, people from all these places attended some of the early meetings held twice a year, which sometimes had attendance near 200. Most of the early meetings were held at Rice or in the Auditorium at the Shell-Westhollow labs. In later years, the meeting was held in nearby places like Austin, College Station, and New Orleans.

What was going on that made the late 60s an optimal time to establish the SWCS? I think the biggest factor was Shell downsizing its labs in Emeryville, CA and moving most its catalysis people to a new research facility at Westhollow. At the same time, Esso was increasing its applied catalysis work both in Baytown 30 miles east of the city and in Baton Rouge. For several years, Phillips Petroleum had been accumulating an amazing number of patents in catalysis at their laboratories in Bartlesville. Bob Eischens came from New York and was applying his pioneering infrared studies at Texaco in Port Arthur. Celanese had several catalysis people doing research near Corpus Christi. Many of you may recall that Texas City was devastated by the largest US chemical plant explosion of an ammonium nitrate ship in the mid-40s. After the explosion, Monsanto rebuilt its facilities there, where workers were doing research on improving catalytic processes for styrene and acrylonitrile manufacture. Petrotex Chemical in



Pasadena, another suburb on Houston's ship channel, was optimizing its butadiene and C₄ olefins production through catalytic processes.

In addition, catalysis groups were springing up at several universities, including surface science by the late John Mike White at the University of Texas, Jack Lunsford's and Wayne Goodman's highly productive groups at Texas A&M, Richard Gonzales at Tulane, Jim Richardson at U of H, Kerry Dooley at LSU, Tom Leland and me at Rice, and groups at other universities in the 5-state area. What was lacking? There was no formal mechanism for these diverse groups to exchange information or get advice in the southwest. The time was ripe for an organization where catalysis could be openly discussed. Although much catalysis research is proprietary, enough was sufficiently open to create a stimulating environment for sharing mutual interests, many focusing on new ultra-high vacuum analytical equipment that was being rapidly developed.

The first thing we did was to organize an NSF-supported workshop at Rice which (not surprisingly) concluded that more funding was needed for research on catalysts for fuels, environmental protection (cat converters), chemicals, etc. At that time, demand was also great for new employees with catalysis training, but the supply was quite limited. This provided an occasion for the development of short courses to train industrial employees in heterogeneous catalysis. Several courses were started around the country. One of the most successful was started at Rice and has continued for more than 30 years through the University of Houston. It can be said, then, that **SWCS was instrumental in starting these heterogeneous catalysis short courses.**

The "Club" was soon invited to join the other half dozen Clubs as a part of the growing North American Catalysis Society. Being the new kid on the block, our Club was asked to host its first biennial North American Meeting (NAM-2) in February 1971, which was held at the Astrodome Hotel in Houston. Jim Richardson and I were Associate and General Chair of the meeting, while Paul Venuto (Mobil Research/Development and a colleague of the late Heinz Heinemann) was in charge of the Program. At that meeting the late Dr. R. J. Kokes (one of my professors at Johns Hopkins) and Dr. H. S. Bloch (Universal Oil Products) were recipients, respectively, of the first Paul H. Emmett and Eugene J. Houdry Awards in fundamental and applied catalysis.

In 1985, the Southwest Catalysis Society was again called on to host a five-day 9th North American Meeting (NAM-9) at Houston's Adam's Mark Hotel. This time, Jack Lunsford and Lynn Slaugh were General and Vice Chair; I was Technical Program Chair. Most recently, the SWCS members organized the spectacular North American Meeting at Houston's downtown Hilton Americas Hotel in 2007, attended by over 1000 delegates from all over the world, "Celebrating Catalysis Texas Style." Kudos again to SWCS officers Kerry Dooley, Brendan Murray, Scott Mitchell, Michael Reynolds, Yun-Feng Chang, Michael Wong, and many, many others! **All told, the SWCS has hosted 3 national events now: 1971 (NAM-2), 1985 (NAM-9) and 2007 (NAM-20).**

Rice University Campus Map



Building numbers

20: Duncan Hall (meeting site)

57: Rice Memorial Center (student center)

44: Central Campus Garage